Bipyridine - Porphyrin Conjugates

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Abstract

The research carried out for this thesis comprises an investigation into the synthesis of bipyridyl-bridged porphyrin compounds and their metal complexes.

Chapter One introduces the bipyridine ligand and summarises research carried out on the functionalisation of 2,2'-bipyridine (bpy). A proposal for a novel study involving the connection of porphyrin functionalities to bpy *via* vinylic linking groups is discussed, and the Wittig methodology proposed to achieve this is described.

Chapter Two outlines the synthesis of the 4,4'-diformyl-2,2'-bipyridine ligand necessary for the Wittig reaction to form the primary target compound, a bipyridyl-bridged bisporphyrinyl ligand. Synthesis of the bipyridine dialdehyde ligand had previously been reported *via* a four step procedure from 4,4'-dimethyl-2,2'-bipyridine in reasonable yield, a result which was unable to be reproduced. The methodology involved an oxidation of the dimethyl bipyridine to the corresponding dicarboxylic acid, esterification to the dimethylester, reduction to form the dialcohol, followed by an oxidation to the desired dialdehyde ligand. All attempts at this procedure, using various reagents for the final oxidation step, were either unsuccessful or resulted in very low yields of product. Thus an alternative single step SeO_2 oxidation of 4,4'-dimethyl-2,2'-bipyridine to form the target dialdehyde was explored. Optimisation of this procedure gave an efficient one step synthesis of 4,4'-diformyl-2,2'-bipyridine, **4**.

Chapter Three discusses the synthesis of the porphyrin phosphonium salt, the second precursor required for this work. Tetra-*meso*-substituted porphyrin moieties were used so that the phosphonium salt appendage would be connected through one of the pyrrolic carbon atoms. A *meso*-tetraphenylporphyrin (TPP) phosphonium salt **5**, had been synthesised in these laboratories, thus the synthetic methodology previously developed was repeated to make this Wittig precursor. The synthesis of a second, more soluble *meso*-tetraxylylporphyrin (TXP) phosphonium salt, **13**, was also developed (an eight step synthesis from mesitylene and pyrrole) and optimised so as to improve the solubility of the resulting bpy compounds.

Application of the Wittig reaction using dialdehyde **4**, and the TPP phosphonium salt **13**, is discussed in Chapter Four. Both the monomeric 4-(*trans*-2"-vinyl-TPPyl)-4'-formyl-2,2'-bipyridine, **14**, and the dimeric 4,4'-(*trans*-2"-vinyl-TPPyl)-2,2'-bipyridine, **15**, bipyridine-porphyrin conjugates were successfully synthesised. The bipyridine ligand is connected to

the porphyrin through a vinylic linking group to one of the pyrrolic positions (2-position) of the porphyrin ring. Bisporphyrinyl ligand **15**, as expected, proved to be insoluble in organic solvents. Before continuing with the more soluble TXP phosphonium salt **13**, some test metallation reactions were performed using the soluble monomeric porphyrinyl bipyridine ligand **14**. Zinc was inserted into the porphyrin ring to form 4-[(*trans*-2"-vinyl-TPPato)zinc(II)]-4'-formyl-2,2'-bipyridine, **16**. Coordination of rhenium to the bipyridyl moiety of the monomeric porphyrin ligand, formed the complex 1,1'-$Re(CO)_3Cl$[4-(*trans*-2"-vinyl-TPPyl)-4'-formyl-2,2'-bipyridine], **17**. A subsequent Wittig reaction was carried out to form the complex 1,1'-$Re(CO)_3Cl$[4,4'-(*trans*-2"-vinyl-TPPyl)-2,2'-bipyridine], **18**.

The remainder of Chapter Four reports the methodology developed for an efficient synthesis of the target bipyridyl-bridged dimeric porphyrin ligand 4,4'-(*trans*-2"-vinyl-TXPyl)-2,2'-bipyridine, **20**, using the tetraxylylporphyrin phosphonium salt, TXP-CH_2PPh_3Cl, **13**. Ligand **20** was first synthesised in two steps. Connection of one porphyrin ring to 4,4'-diformyl-2,2'-bipyridine **4**, formed the monomeric porphyrin ligand, 4-(*trans*-2"-vinyl-TXPyl)-4'-formyl-2,2'-bipyridine, **19**. A second Wittig reaction on this ligand resulted in the target bisporphyrinyl compound. A more efficient one step Wittig reaction was then investigated, resulting in a high yielding single step preparation of bisporphyrinyl bipyridine **20**.

Coordination of the metal ions Mo, Re, and Ru, to the bipyridyl moiety of the target bipyridyl-bridged tetraxylylporphyrin dimer **20**, are described in Chapter Five. A monoporphyrinyl molybdenum-bound bipyridine complex, 1,1'-$Mo(CO)_4$[4-(*trans*-2"-vinyl-TXPyl)-4'-formyl-2,2'-bipyridine], **22**, was synthesised *via* a Wittig reaction from the bipyridyl molybdenum complex 1,1'-$Mo(CO)_4$[4,4'-diformyl-2,2'-bipyridine], **21**. The rhenium-bound bisporphyrinyl complex, 1,1'-$Re(CO)_3Cl$[4,4'-(*trans*-2"-vinyl-TXPyl)-2,2'-bipyridine], **23** was synthesised in a single step metallation reaction of the bisporphyrinyl bipyridine **20** with rhenium pentacarbonyl chloride. A bisporphyrinyl ruthenium(II) bipyridine complex 1,1'-$Ru(CO)_2Cl_2$[4,4'-(*trans*-2"-vinyl-TXPyl)-2,2'-bipyridine], **25**, was synthesised in a one step Wittig reaction from the Ru(II)bpy complex 1,1'-$Ru(CO)_2Cl_2$[4,4'-diformyl-2,2'-bipyridine], **24**. The synthesis and characterisation of a tetraporphyrinyl ruthenium(II)bisbipyridine complex is also reported. 1,1'-$RuCl_2$[bis-4,4'-(*trans*-2"-vinyl-TXPyl)-2,2'-bipyridine], **27**, was synthesised *via* a single step metallation reaction between bisporphyrinyl bipyridine **20** and a $RuCl_2(DMSO)_4$ complex.

Chapter Six contains a brief summary of the results obtained throughout this study and future work to be done in this area.

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Abbreviations

amu	Atomic mass units
Bpy	2,2'-Bipyridine
CT	Charge transfer
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
FAB	Fast Atom Bombardment
h	Hours
^{1}H NMR	Proton Nuclear Magnetic Resonance Spectroscopy
HRMS	High Resolution Mass Spectrometry
LDA	Lithium diisopropylamide
LMCT	Ligand-to-metal charge transfer
mins	Minutes
MLCT	Metal-to-ligand charge transfer
MnP	Manganese peroxidase
NLO	Non-linear optical
RT	Room temperature
tlc	Thin Layer Chromatography
TPP	5,10,15,20-Tetraphenylporphyrin (*meso*-tetraphenylporphyrin)
TXP	5,10,15,20-Tetra(3,5-dimethylphenyl)porphyrin (*meso*-tetraxylylporphyrin)
UV/Vis	Ultraviolet/Visible Spectroscopy
Xy	3,5-Dimethylphenyl (xylyl)